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14. ABSTRACT

The focus of this challenge project is on theoretical studies of ionic liquids as advanced monopropellants for rocket, missile, and satellite propulsion applications. Ionic liquids offer several advantages over conventional monopropellants such as hydrazine, including higher energy content, higher densities, very low vapor pressures, and reduced vapor toxicities. They are likewise well suited for use as working fluids in electric propulsion devices. The properties of ionic liquids may be tuned via the choice of component ions and their chemical substituents, so that they may be optimized for specific applications.

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Design of Energetic Ionic Liquids (Challenge Project C2H) [PREPRINT]
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Introduction

The focus of this challenge project is on theoretical studies of ionic liquids as advanced monopropellants for rocket, missile, and satellite propulsion applications. Ionic liquids offer several advantages over conventional monopropellants such as hydrazine, including higher energy content, higher densities, very low vapor pressures, and reduced vapor toxicities. They are likewise well suited for use as working fluids in electric propulsion devices. The properties of ionic liquids may be tuned via the choice of component ions and their chemical substituents, so that they may be optimized for specific applications.

Objective

The objective of this study is the design of new ionic liquids for chemical propulsion applications. Specific objectives include characterization of the structures, energy content, stabilities, combustion and decomposition pathways, and bulk properties of new ionic liquids which are suitable as replacements for hydrazine, a widely used but highly toxic and carcinogenic monopropellant.

Methodology

The expertise of this team ranges from electronic structure theory calculations at the molecular level to molecular dynamics simulations using both ab initio and model potentials. Calculations are performed using a combination of electronic structure theory, classical molecular dynamics, quantum and mixed quantum-classical simulation methods, and coarse-graining simulation techniques.

Results

Systematic studies have been performed on a series of derivatives of pentazolium-based ionic liquids. Molecular structures, heats of formation, and the extent of electron delocalization have been determined for each derivative to identify suitable candidates for synthesis. The effects of hydrogen bonding and proton transfer reactions on the physical properties of these systems have been analyzed. The structures, vibrational spectra, binding energies, and internal energy distributions of a series of gas-phase clusters containing ethylmethyimidazolium cations and bis(trifluoromethylsulfonyl)imide anions have been characterized. Molecular dynamics simulations have been performed to compare polarizable vs. non-polarizable force fields in predicting several key bulk properties such as density and transport coefficients. Simulations of the nanostructural characteristics of ionic liquid/water mixtures have been performed.

Significance to DoD

As the Air Force continues to evolve into an Air and Space Force, reliable and cost effective access to space as well as the control and exploitation of the space environment is becoming of paramount importance. Similar issues impact the other DoD branches as well. Space-based lasers and global networks of microsatellites are two examples of defense systems that could be impacted by the proposed research. An additional payoff is the mitigation of environmental and health hazards associated with space-related operations. *Benefits to the warfighter include cost-effective, more reliable access to space, control and exploitation of space, longer usable lifetimes of space-based assets, and mitigation of environmental and health hazards.*

I. Introduction

The design of new high energy density materials (HEDM), which are more efficient, reliable, and environmentally benign than existing rocket propellants, is a high DoD priority. The focus of this effort has been on the development of new propellants and energetic additives, including highly strained hydrocarbons, polynitrogen compounds, and advanced monopropellants. Some of the issues that must be addressed in theoretical efforts to design new HEDM include an assessment of their energy content, their thermodynamic and kinetic stability, and the design of new synthetic routes to proposed new HEDM that have not yet been synthesized.

A specific area of interest to the DoD is the discovery of a suitable replacement for hydrazine, a widely used monopropellant for low-thrust propulsion applications such as orbital maneuvering and satellite stationkeeping. The desire to replace hydrazine is motivated by several factors. Perhaps the most severe limitation of hydrazine is its carcinogenic nature and extreme respiratory and dermatological toxicity, with correspondingly large costs associated with controlling these environmental and biological hazards. Furthermore, the performance of hydrazine as a monopropellant is rather modest due to its relatively low density and specific impulse compared to a prototypical ionic monopropellant salt such as 4-amino-1,2,4-triazolium dinitramide. The replacement of hydrazine with more energetic, less hazardous energetic monopropellants is clearly needed.

A specific type of HEDM of current interest is derived from a broad class of compounds known generically as ionic liquids (ILs), which are chemical salts with unusually low melting points; e.g., below 100° C. The general interest in ILs has focused mainly on their use as environmentally benign ("green") solvents for a wide range of chemical reactions. Some of the properties of ILs which make them attractive as solvents include their low vapor pressure, large liquid ranges, and thermal stability. The interest in ILs as new monopropellants stems from several factors. For example, the properties of ILs, including their energy content, can be "tuned" through a judicious choice of component ions and their substituents. Furthermore, the virtually nonexistent vapor pressure of ILs greatly reduces the environmental and biological hazards due to respiratory and dermatological toxicity. Finally, the densities of ILs generally are significantly greater than those of conventional liquid monopropellants such as hydrazine.

Although there have been extensive experimental studies of chemical reactions in ILs, little has been done in the area of characterization of the fundamental chemical and physical properties of ILs. In particular, one of the most pressing needs in the broader area of IL development, and particularly in the design of energetic ILs, is the application of robust theoretical methods for the reliable prediction of IL heats of formation, synthesis routes, phase transitions, ion conformations, thermal stabilities, densities, and viscosities. The focus of this study is on the characterization, design, and synthesis of the next generation of monopropellants for rocket propulsion applications.

II. Computational Methods

An integrated approach utilizing multiple computational methods is used to predict and characterize the intrinsic and bulk properties of energetic ionic liquids. At the molecular level, highly accurate electronic structure methods are used to predict the fundamental properties of the ionic liquid components, including molecular structures, charge delocalization, heats of formation, and proton transfer reaction pathways and barriers. Geometries, electronic structures, and properties (including heats of formation) of the component ions are predicted using second-order perturbation theory (MP2, also known as MBPT(2)[1]), density functional theory (DFT)[2], and the "Gaussian-N" (GN)[3] methods. The Nuclear-Electronic Orbital (NEO)[4] approach is used for capturing the quantum dynamical effects of hydrogen bonding and proton transfer. In addition, the complex spectrum of ionic liquid physical properties requires utilization of polarizable force fields in condensed phase simulations in order to obtain reliable predictions of many key bulk properties.

III. Results and Discussion

A systematic study[5] has been carried out on a series of substituted pentazole-based cations, including predictions of the molecular structures, heats of formation and extent of electron delocalization. The 1H,3R isomers were found to be approximately 20 kcall/mol more stable than the corresponding 1H, 2R structures. It was also determined that the 1H,1R isomers are all unstable, spontaneously leading to formation of one or more nitrogen molecules and a cationic fragment. The contributions of the primary resonance structures in the parent 1H,2H and 1H,3H cations were found to be roughly equal, indicating that the excess positive charge is highly delocalized in the ring. The small geometry changes in the rings in the derivative cations suggests that substitution does not

significantly change the degree of charge delocalization. It appears that substitution will not hinder the ability of these cations to form ionic liquids.

Heats of formation: The gas-phase heats of formation have been computed using a combination of G2 theory[3] and isodesmic reactions[6], as described in detail elsewhere[5], and are summarized in Table 1. The heat of formation of the un-substituted 1,3 (1,2) cation is 286.5 (303.9) kcal/mol. Most substituents increase this value, the exceptions being -CH₃, -OH, -CH₂NO₂, and –OCH₃. The largest increases in heat of formation occurs for –CN and -N₃. These results are similar to those found in previous studies of substituted triazolium[7] and tetrazolium[8] cations.
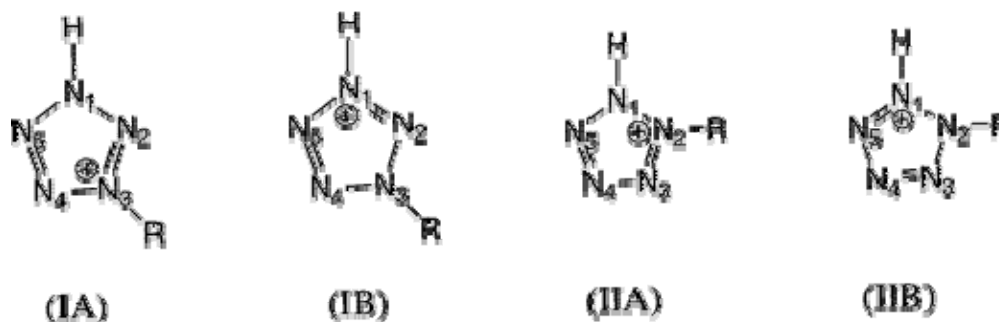

(IA)   (IB)   (IIA)   (IIB)

Table 1: Heats of Formation at 298 K for Gas-Phase Monosubstituted 1H,3R- and 1H,2R-Pentazole Cations[a]							
	1H,3R-isomer				1H,2R-isomer			
R	ΔH_f° (IA) (kcal/mol)	ΔH_f° (IB) (kcal/mol)	average (kcal/mol)	average (kcal/g)	ΔH_f° (IIA) (kcal/mol)	ΔH_f° (IIB) (kcal/mol)	average (kcal/mol)	average (kcal.g)
H	285.6	285.6	285.6	4.0	303.9	303.9	303.9	4.2
F	307.9	307.2	307.6	3.4	328.5	327.8	328.2	3.6
CH₃	268.3	267.6	268.0	3.1	284.8	284.2	284.5	3.3
CN	358.1	358.5	358.3	3.7	376.6	377.0	376.8	3.9
NH₂	302.2	301.0	301.6	3.5	318.3	317.1	317.7	3.7
OH	283.7	281.8	282.8	3.2	301.2	299.3	300.3	3.4
CH₂NO₂	278.8	277.9	278.3	2.1	296.1	295.1	295.6	2.2
N₃	393.6	391.0	392.3	3.5	409.2	406.6	407.9	3.6
NF₂	317.3	313.9	315.6	2.6	335.4	332.1	333.7	2.7
C₂H₃	294.6	293.3	294.0	3.0	311.1	309.8	310.5	3.2
OCH₃	278.1	276.4	277.2	2.7	293.9	292.2	293.0	2.9

[a] IA, IB, IIA, and IIB refer to the specific resonance structures shown above, with their average values being the predicted heats (the average is given in both kcal/mol and kcal/g).

Cation Transition States and Decomposition Products: The 1H,3R isomers are found to decompose to N₂ + [HN₃R]⁺ via a single-step mechanism. The energy barriers vary with substituent from 20 to 29 kcal/mol at the CR-CCSD(T) level of theory, as shown in Table 2. In contrast, the decomposition mechanisms of the 1H,2R isomers are more complex, involving two-step processes that likewise result in formation of N₂ + [HN₃R]⁺. The only exception is for R=CH₂NO₂, in which case the 1H,2R decomposition products are N₂ + HONO + [H₂CN₃]⁺. The barriers for

the first step of the 1H,2R decomposition pathways range from 22 to 36 kcal/mol as a function of substituent, whereas the barriers for the second step range from 6 (R=N$_3$) to 58 (R=NH$_2$) kcal/mol, at the CR-CCSD(T) level (see Table 2.)

Table 2: Activation Energies (E_a) for the Decomposition of Protonated Pentazole To Form the Corresponding Azidinium Cations and N$_2$ (Including Zero-Point Energy Correction, in kcal/mol)[a]

	1,3-Isomer		1,2-Isomer			
	E_a		E_{a1}		E_{a2}	
	MP2	CR-CCSD(T)	MP2	CR-CCSD(T)	MP2	CR-CCSD(T)
H	24.2	28.2	30.3	30.9	46.8	46.1
F	22.6	24.2	19.3	22.1	36.7	37.5
CH$_3$	24.0	28.8	37.0	35.6	56.9	53.9
CN	19.0	22.4	19.0	22.3	37.3	39.3
NH$_2$	18.7	22.6	30.5	24.6	50.5	57.8
OH	19.9	22.0	23.6	24.6	33.5	40.2
CH$_2$NO$_2$	22.6	26.8	28.6	30.7	17.9	13.6
N$_3$	16.0	20.2	23.4	25.2	14.1	6.4
NF$_2$	19.7	23.3	21.0	23.4	34.2	39.3
C$_2$H$_3$	21.8	26.8	32.0	31.1	42.4	50.8
OCH3	18.7	21.9	25.7	26.8	3.2	16.0

[a]Subscripts 1 and 2 label the first and second activation energies, respectively, for the 1,2-isomer. E_{a2} is calculated relative to the final decomposition products.

Proton Transfer: When a cation is paired with an oxygen-rich anion, a single gas phase ion pair is not generally found to be stable. A proton transfers with little or no barrier from the cation to the anion to form a neutral pair, suggesting that proton transfer is a key step in the decomposition of protonated pentazoles. The largest barrier found in this study was ~6 kcal/mol, at the MP2/6-311G(d,p) level of theory, for the 1H,3H pentazolium-dinitramide pair. The 1H,3H cation paired with perchlorate (nitrate) has a proton transfer barrier of 2.7 (3.0) kcal/mol.

[Emim$^\pm$][Im$^-$] Ion Clusters: Ionic liquids such as 1-ethyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ([Emim$^+$][Im$^-$]) show great promise as advanced working fluids in electric propulsion applications. In order to assess and tune the performance of these types of working fluids, it is necessary to characterize the exhaust plume, which contains a distribution of clusters such as [Emim$^+$]$_m$[Im$^-$]$_{m\pm1}$; i.e., containing either an excess cation or anion. The gas-phase structures, harmonic vibrational frequencies, binding energies, and internal thermal energy distributions of a series of ion clusters [Emim$^+$]$_m$[Im$^-$]$_{m\pm1}$ (m=1-3) were computed using the hybrid B3LYP density functional and the 6-311++G(d,p) basis set. The computed structures and scaled harmonic frequencies were used to calculate the temperature-dependent internal thermal energy distributions, as illustrated in Figure 1 for the [Emim$^+$][Emim-Im] and [Im$^-$][Emim-Im] ion clusters, and compared to experimental mass spectrometric measurements of ion cluster abundances. The shift in the theoretical internal energy distributions to higher energies as a function of temperature suggest that the population of these ion clusters in the gas phase should decrease with increasing temperature. In the case of the [Im$^-$][Emim-Im] cluster, however, the experimental ion mass spectra show the abundance of the [Im$^-$][Emim-Im] cluster has a minimal temperature dependence. This suggests that additional factors such as rapid dissociation of larger clusters to form evaporatively cooled [Im$^-$][Emim-Im] clusters may be important.
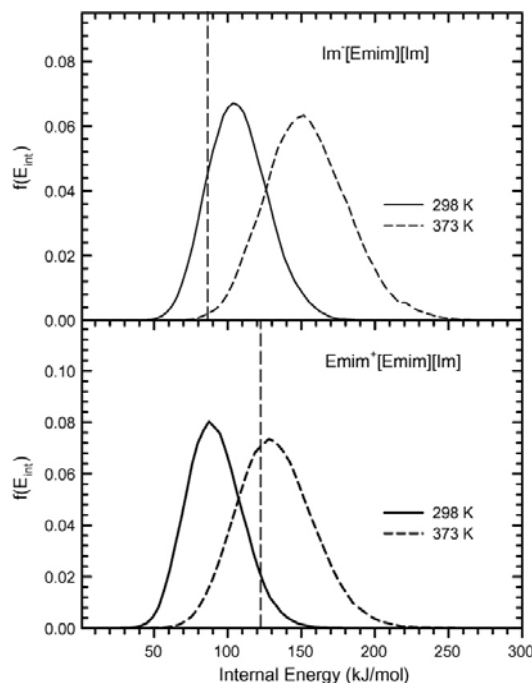
Figure 1. Calculated thermal internal energy distributions at 298 and 373K for Im−[Emim][Im] (top) and Emim+[Emim][Im] (bottom). The vertical dashed lines represent the dissociation limits of the respective cluster ions.

Bulk Propeties: An electronically polarizable force field[9] for ionic liquids (IL) has been developed by the Voth group, based on Thole's smearing dipole model[10], in which each atomic site is treated as a polarizability center and the anisotropic molecular polarizability may be reproduced through the interaction among the atomic sites. In molecular dynamics (MD) simulations, the induced dipole is propagated by the extended Lagrangian method.[11]

Our molecular dynamics study[12] of 1-hydroxyethyl-4-amino-1,2,4-triazolium nitrate (HEATN) have identified a glass transition temperature region around 275K, in agreement with experiment.[13] Various other physical properties of liquid state were intensively studied at 400 K. The viscosity was fitted as 64.25 and 38.21 c.p., by the nonpolarizable and polarizable models[9], respectively, as shown in Figure 2. A study of structural properties of liquid/vacuum interface shows that there is vanishing layering at the interface, in accordance with the poor ion packing. The calculated surface tension is 68.37 ± 2.98 mN/m and 93.91 ± 2.43 mN/m, for the nonpolarizable and polarizable model, respectively.[12]
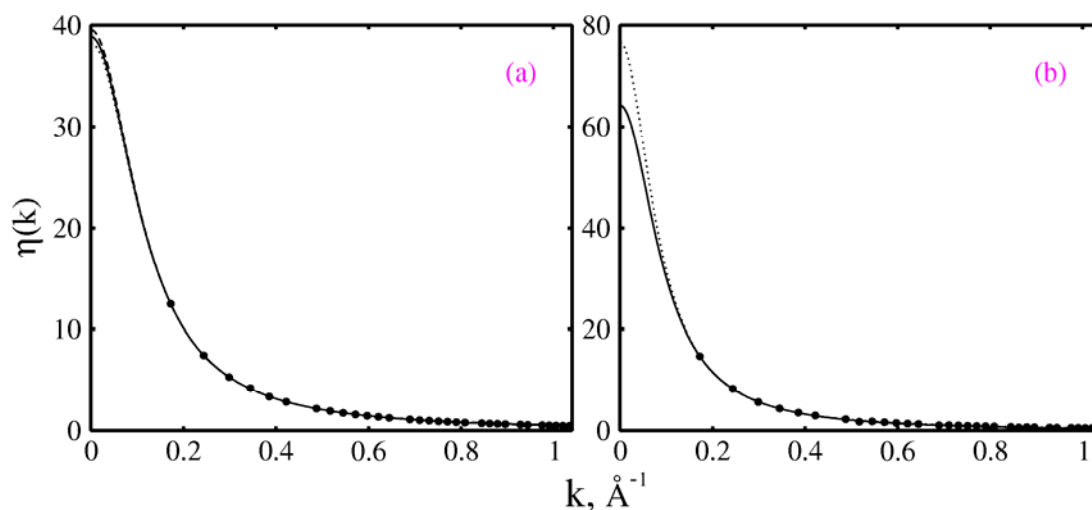
**Figure 2. Calculated viscosity curves of HEATN at T=400K, using (a) polarizable and (b) nonpolarizable force fields.**

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Nanostructural Organization in Ionic Liquid/Water Mixtures:
Atomistic molecular dynamics simulations utilizing the standard Amber force field[15] have been performed on a series of mixtures of 1-octyl-3-methylimidazolium nitrate ionic liquid and water. The nitrate anion, the aromatic ring of the cation, and the single methyl group bonded to the ring were designated the polar groups and are shown as red in Figure 3. The whole alkyl chain was defined as the nonpolar group and colored yellow, and the water molecules are shown as dark blue. These simulations show that, within the range of water contents examined, polar networks, water networks and micelles possess an approximately invariant characteristic length at around 20Å. Furthermore, as the amount of water increases, the polar network is continuously broken up (screened) by the intruding water, while the structural organization of the water network and the micelle exhibits a *turnover*, as shown in Figure 4. The turnover of structural organization of micelles results from the persistent competition between the hydrophobic interactions of the nonpolar groups and the break up of the charged polar network with increasing water content, while the turnover of the water network results from the competition between the water-water and water-anion interactions.[14]
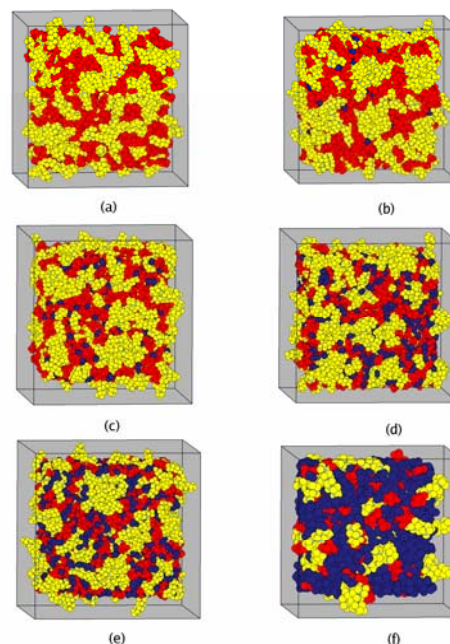
Figure 3. Snapshots of six selected simulation cells, taken from the MD trajectory data. The polar groups, nonpolar groups, and water are colored red, yellow, and dark blue, respectively. (a) Dry IL sample, (b) mixture with water of 20% mole fraction, (c) 50% mole fraction, (d) 75% mole fraction, (e) 80% mole fraction, (f) 95.2% mole fraction.

Hydrophobic Behavior of Non-polar Molecules in Ionic Liquids: Figure 4 shows the aggregation of methane molecules in 1-butyl-3-methylimidiazolium chloride ionic liquid ($BMIM^+/CL^-$). The chloride anion, the aromatic ring of the cation, and the single methyl group bonded to the ring were designated the polar groups and are shown as red. The whole butyl chain was defined as the nonpolar group and colored yellow, and the methane molecules are shown as dark blue. The aggregation of nonpolar molecules decreases with increasing symmetries of the anions, or equivalently, decreases with decreasing strength of electrostatic attraction between polar head/anion groups. For a given anion, the aggregation decreases with increasing length of the side chain. A comparison between methane and butane shows that methane molecules have much stronger aggregation tendency than butane. The above results[16], together with the polar/nonpolar phase separation in pure ionic liquids, can be explained by a unified entropic origin.[17]
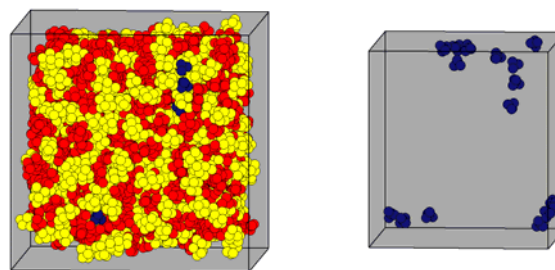
Figure 4. Snapshot of BMIM+/CL- simulation cell, taken from the MD trajectory data. The polar groups, nonpolar groups, and methane are colored red, yellow, and dark blue, respectively. In the panel on the right, the polar and nonpolar groups have been removed in order to reveal the positions of all the methane molecules.

IV. **Summary and Conclusions**

The geometries, electronic structures, and heats of formation of a series of substituted pentazole-based cations have been predicted using quantum chemical methods. The 1H,3R isomers are found to be approximately 20 kcal/mol more stable than 1H,2R, whereas all of the 1H,1R spontaneously decompose to form one or more nitrogen molecules and a fragment cation. Electron-donating substituents such as methyl, hydroxyl, methoxy, and nitromethyl groups lower the heat of formation relative to the unsubstituted cation. The opposite behavior is

observed for electron-withdrawing groups, with cyano (-CN) and azido ($-N_3$) groups yielding the largest increases in the heat of formation. The 1H,3R isomers decompose to form N_2 + $[HN_3R]^+$ by a one-step mechanism, whereas the 1H,2R isomer decomposition involves two steps connected by an open-ring intermediate. The gas-phase proton transfer reactions of the 1H,2R/1H,3R cations with dinitramide, perchlorate, and nitrate anions have been calculated. At the MP2/6-311++G(d,p) level of theory, the energy barriers for these reactions are found to be small (< ~6 kcal/mol) or nonexistent, suggesting that proton transfer is a key step in the decomposition of these ionic liquids.

The structures, harmonic vibrational frequencies, binding energies, and internal thermal energy distributions of gas-phase ion clusters of the 1-ethyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ionic liquid have been predicted using density functional theory (B3LYP/6-311++G(d,p)).   The calculated internal energy distributions predict a temperature dependence of the population of the [Im⁻][Emim-Im] ion clusters, but not seen in mass spectrometric experiments. This suggests that additional effects such as rapid dissociation of larger clusters to form evaporatively cooled [Im⁻][Emim-Im] clusters may be important.

Classical molecular dynamics simulations of HEATN predict the presence of a glass transition at a temperature of about 275 K, in agreement with experiment.   Utilization of a polarizable versus a nonpolarizable force field resulted in significant differences in predicted transport properties such as self-diffusion coefficients and shear viscosity. Simulations of 1-octyl-3-methylimidazolium nitrate ionic liquid/water mixtures show that as the amount of water increases, the polar network is continuously disrupted by the intruding water, while the structural organization of the water network and the micelle exhibits a "turnover." In contrast, simulations of methane in $[BMIM]^+[Cl]^-$ show that aggregation of nonpolar molecules decreases with increasing symmetries of the anions, or equivalently, decreases with decreasing strength of electrostatic attraction between polar head/anion groups.

References

1. C. Moller, M. S. Plesset, *Phys. Rev.* **1934,** *46,* 618; J. A. Pople, J. S. Binkley, R. Seeger, *Int. J. Quantum Chem. S10,* **1976**, 1; M. J. Frisch, M. Head-Gordon, J. A. Pople, *Chem.Phys.Lett.* **1990**, *166*, 275.;. R. J. Bartlett, D. M. Silver, *Int. J. Quantum Chem. Symp.* **1975,** *9,* 1927.

2. A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; P. J. Stephens, F. J. Devlin, C. F. Chablowski, M. J. Frisch, *J. Phys. Chem.* **1994,** 98, 11623; R. H. Hertwig, W. Koch, *Chem. Phys. Lett*. **1997**, 268, 345.; S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, 58, 1200.

3. See, for example, L.A. Curtiss, K.Raghavachari, G.W. Trucks, and J.A. Pople *J. Chem. Phys.* **1991,** 94, 7221.

4. See, for example, C.Swalina; M.V. Pak; and S.Hammes-Schiffer, *J. Chem. Phys*. **2005**, 123, 14303.

5. I.S.O. Pimienta, S. Elzey, J.A. Boatz, and M.S. Gordon, *J. Phys. Chem. A.;* **2007**, 111, 691.

6. W.J. Hehre; R. Ditchfield; L. Radom; J.A. Pople, J. A. *J. Am. Chem. Soc.* **1970**, 92, 4796.

7. M.W. Schmidt; M.S. Gordon; J.A. Boatz, *J. Phys. Chem. A.;* **2005**, 109, 7285.

8. D.D. Zorn; J.A. Boatz; M.S. Gordon, *J. Phys. Chem. B.,* **2006**, 110, 11110.

9. T. Yan; C.J. Burnham; M.G. Del Pópolo; G.A. Voth, *J. Phys. Chem. B* **2004,** 108, (32), 11877.

10. B.T. Thole, *Chem. Phys.* **1981,** 59, 341.

11. M.-L. Saboungi; A. Rahman J.W. Halley; M. Blander, *J. Chem. Phys.* **1998,** 88, 5818.

12. W. Jiang, T. Yan, Y. Wang, G. A. Voth (to be submitted).

13. *Private communication with Air Force Research Lab.* **2006**.

14. Jiang, W.; Wang, Y.; Voth, G. A. *J. Phys. Chem. B.* **2007**, 111, 4812.

15. Cornell, W. D.; Cieplak, P.; Bayly, C. I.; Gould, I. R.; Merz, K. M.; Ferguson, D. M.; Spellmeyer, D. C.; Fox, T.; Caldwell, J. W.; Kollman, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 5179.

16. Jiang, W.; Voth, G. A. *in preparation* **2007**.

17. Chandler, D. *Nature* **2005**, *437*, 640.